Stable Isotope Tracers

OCN 623 – Chemical Oceanography

21 March 2017

Reading: Emerson and Hedges, Chapter 5, p.134-153

Student Learning Outcomes

At the completion of this class, students should be able to:

1. Explain and use the *"delta" notation* commonly utilized with stable isotopes
2. Explain *isotopic fractionation* and how it can be used to elucidate oceanographic phenomena
3. Describe the common uses of stable isotopes as *oceanic tracers*

Outline

- Stable Isotopes - Introduction & Notation
- Isotope Fractionation
- Some Oceanographic Applications

Uses of Stable Isotopes in Oceanography

- Most commonly studied:
  - ^{2}H ^{3}He ^{13}C ^{15}N ^{18}O ^{34}S
- Tracers of biological, chemical, geological ocean processes
- Water-mass characterization and tracing
- Paleoceanography - Record past changes in the ocean
- Pulse/chase experiments - Determine metabolic rates and pathways (labeled tracers)

Isotopes of Elements

The chemical characteristic of an element is determined by the number of protons in its nucleus.

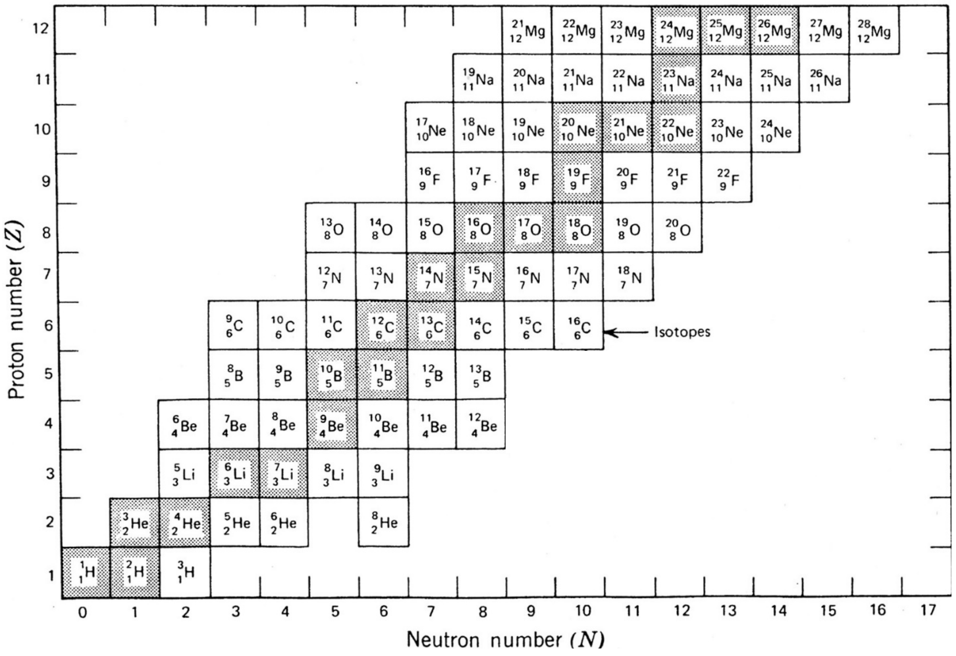
Atomic Number (Z) = number of protons = defines the chemistry

Atomic Mass (N) = protons + neutrons

Isotopes = atoms with same Z but different N

Abbreviated: *^{12}C, ^{13}C, ^{14}C* *or* *C-12, C-13, C-14*

Nuclides of Elements 1 (Hydrogen) through 12 (Magnesium)



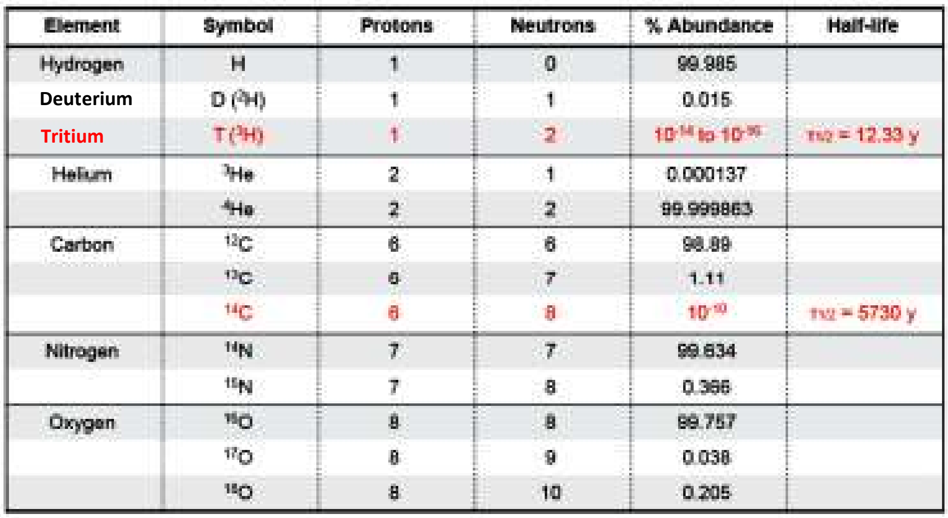
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
12										$^{21}_{12}Mg$	$^{22}_{12}Mg$	$^{23}_{12}Mg$	$^{24}_{12}Mg$	$^{25}_{12}Mg$	$^{26}_{12}Mg$	$^{27}_{12}Mg$	$^{28}_{12}Mg$	
11									$^{19}_{11}Na$	$^{20}_{11}Na$	$^{21}_{11}Na$	$^{22}_{11}Na$	$^{23}_{11}Na$	$^{24}_{11}Na$	$^{25}_{11}Na$	$^{26}_{11}Na$		
10								$^{17}_{10}Ne$	$^{18}_{10}Ne$	$^{19}_{10}Ne$	$^{20}_{10}Ne$	$^{21}_{10}Ne$	$^{22}_{10}Ne$	$^{23}_{10}Ne$	$^{24}_{10}Ne$			
9								$^{16}_{9}F$	$^{17}_{9}F$	$^{18}_{9}F$	$^{19}_{9}F$	$^{20}_{9}F$	$^{21}_{9}F$	$^{22}_{9}F$				
8						$^{13}_{8}O$	$^{14}_{8}O$	$^{15}_{8}O$	$^{16}_{8}O$	$^{17}_{8}O$	$^{18}_{8}O$	$^{19}_{8}O$	$^{20}_{8}O$					
7						$^{12}_{7}N$	$^{13}_{7}N$	$^{14}_{7}N$	$^{15}_{7}N$	$^{16}_{7}N$	$^{17}_{7}N$	$^{18}_{7}N$						
6				$^{9}_{6}C$	$^{10}_{6}C$	$^{11}_{6}C$	$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{6}C$	$^{15}_{6}C$	$^{16}_{6}C$	← Isotopes						
5				$^{8}_{5}B$	$^{9}_{5}B$	$^{10}_{5}B$	$^{11}_{5}B$	$^{12}_{5}B$	$^{13}_{5}B$									
4			$^{6}_{4}Be$	$^{7}_{4}Be$	$^{8}_{4}Be$	$^{9}_{4}Be$	$^{10}_{4}Be$	$^{11}_{4}Be$	$^{12}_{4}Be$									
3			$^{5}_{3}Li$	$^{6}_{3}Li$	$^{7}_{3}Li$	$^{8}_{3}Li$	$^{9}_{3}Li$											
2		$^{3}_{2}He$	$^{4}_{2}He$	$^{5}_{2}He$	$^{6}_{2}He$		$^{8}_{2}He$											
1	$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$															

Proton number (Z)

Neutron number (N)

Most elements have more than one stable isotope (shaded)

Most Commonly Used Isotopes



Element	Symbol	Protons	Neutrons	% Abundance	Half-life
Hydrogen	H	1	0	99.985	
Deuterium	D (^2H)	1	1	0.015	
Tritium	T (^3H)	1	2	10^{-14} to 10^{-16}	$t_{1/2}$ = 12.33 y
Helium	^3He	2	1	0.000137	
	^4He	2	2	99.999863	
Carbon	^{12}C	6	6	98.89	
	^{13}C	6	7	1.11	
	^{14}C	6	8	10^{-10}	$t_{1/2}$ = 5730 y
Nitrogen	^{14}N	7	7	99.634	
	^{15}N	7	8	0.366	
Oxygen	^{16}O	8	8	99.757	
	^{17}O	8	9	0.038	
	^{18}O	8	10	0.205	

% abundance is for the average Earth's crust, ocean and atmosphere

Red isotopes
are
radioactive

All isotopes of a given element have the same basic chemical properties, yet heavier isotopes typically form stronger bonds and diffuse slightly slower

The "Delta" Notation

- Absolute isotope ratios are measured for samples and a standard, and the relative measure "delta" is calculated:

$$\delta^{13}C \equiv \frac{(^{13}C/^{12}C)_{Sample} - (^{13}C/^{12}C)_{Standard}}{(^{13}C/^{12}C)_{Standard}} \cdot 1000\,‰$$

- ‰ = per mil = 10^{-3} Example: 0.005 = 5‰

- Samples with negative delta values are *depleted in ^{13}C* (they are "*light*")
- Samples with positive delta values are *enriched in ^{13}C* (they are "*heavy*")

Each isotopic measurement is reported relative to a standard:

Element	δ value	Ratio	Standard
Hydrogen	δD	$^{2}H/^{1}H$	Standard Mean Ocean Water (SMOW) ←
			Standard Light Antarctic Precipitation (SLAP2)
Helium	$\delta^{3}He$	$^{3}He/^{4}He$	Atmospheric He ←
Boron	$\delta^{11}B$	$^{11}B/^{10}B$	NIST SRM 951
Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	Pee Dee Belemnite (PDB)
Nitrogen	$\delta^{15}N$	$^{15}N/^{14}N$	Atmospheric N_2 ←
Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	Standard Mean Ocean Water (SMOW) ←
			Standard Light Antarctic Precipitation (SLAP2)
			Pee Dee Belemnite (PDB)
	$\delta^{17}O$	$^{17}O/^{16}O$	Standard Mean Ocean Water (SMOW) ←
Sulfur	$\delta^{34}S$	$^{34}S/^{32}S$	Canyon Diablo Troilite (CDT)

Equilibrium Isotopic Fractionation

Fractionation occurs in reactions that do not go to completion:

- Lighter isotopes react faster, and to a greater extent
- Reactants are enriched in the heavier isotopes
- Reaction products are depleted in the heavier isotopes

Note: There is no equilibrium fractionation if a reaction goes to completion (*i.e.*, all of the reactants are consumed)

Fractionation Factor (α): $\alpha_{A/B} = R_{Prod} / R_{React}$

where R_{Prod} and R_{React} are the isotope ratios of the Product and the Reactant after equilibrium is reached (Reactant ↔ Product)

Kinetic Isotopic Fractionation

Unidirectional reactions (*e.g.*, those involving organic matter) show kinetic fractionation

Example: $^{12}CO_2 + H_2O \rightarrow {}^{12}CH_2O + O_2$ *faster*
$^{13}CO_2 + H_2O \rightarrow {}^{13}CH_2O + O_2$ *slower*

Thus, organic matter gets depleted in ^{13}C during photosynthesis (*i.e.*, $\delta^{13}C$ becomes more negative)

Similarly, organic matter gets enriched in ^{13}C during respiration (*i.e.*, $\delta^{13}C$ becomes more positive):

$^{12}CH_2O + O_2 \rightarrow {}^{12}CO_2 + H_2O$ *faster*
$^{13}CH_2O + O_2 \rightarrow {}^{13}CO_2 + H_2O$ *slower*

Group Discussion

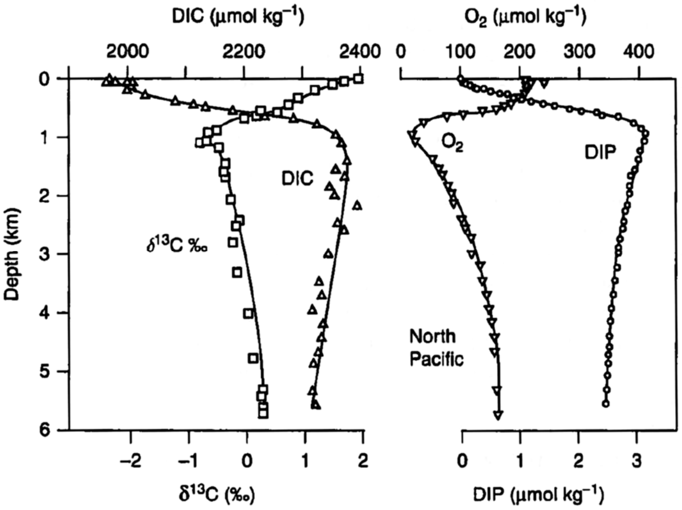


Figure 5 7 A profile of the $\delta^{13}C$ of DIC in the Pacific Ocean showing the surface enrichment and the correlation with DIC, O_2 and dissolved inorganic phosphorus (DIP). Redrawn from Broecker and Peng (1982).

Why is the $\delta^{13}C_{DIC}$ curve the shape it is? What processes are important? (Prepare an explanation of your interpretation)

Examples of Stable Isotopes in Oceanography

- ^{3}He to study deep ocean circulation in the Pacific
- ^{18}O to determine freshwater balance in the Arctic Ocean
- ^{18}O as a paleotemperature recorder

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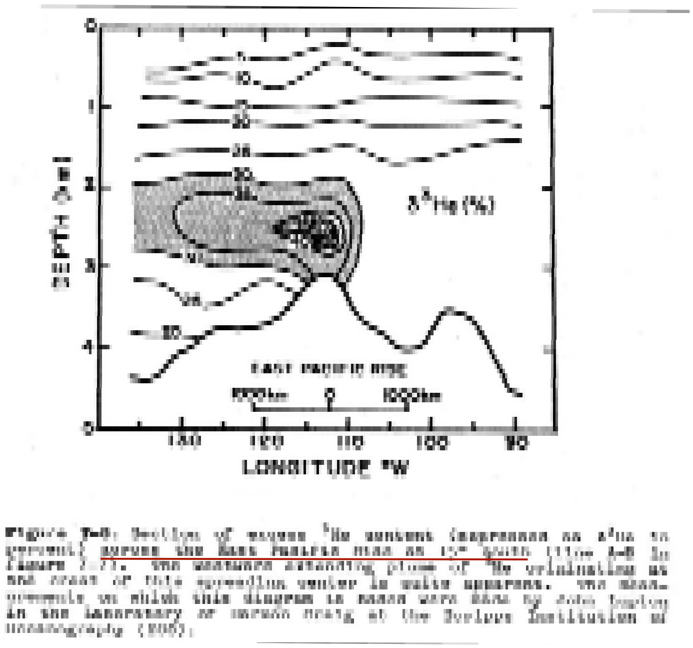
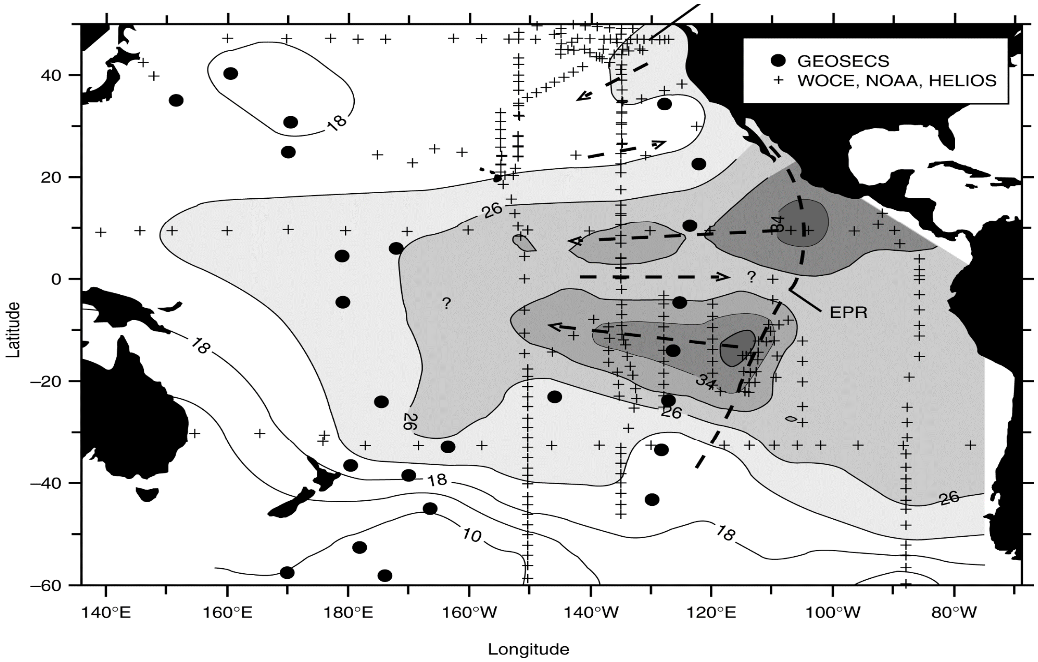
^{3}He Plume from East Pacific Rise



Broecker and Peng, 1982

^{3}He (%) at 2500 m depth



J. Lupton

^{3}He Plume from Loihi Seamount (Hawaii)

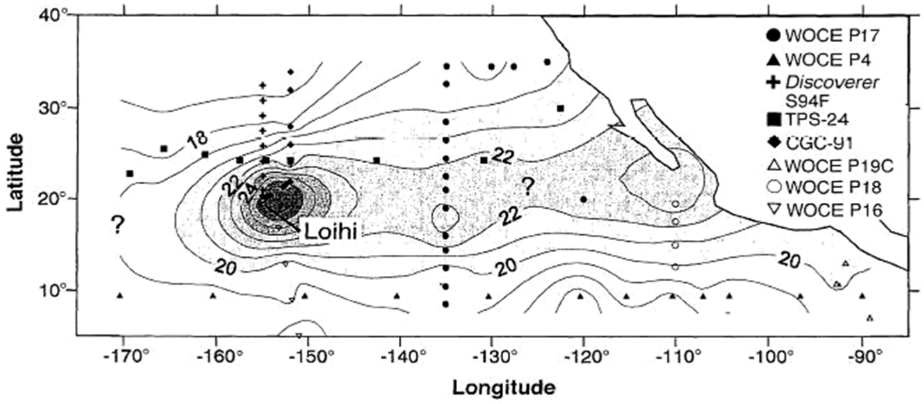


Fig. 6. δ(^{3}He)% contoured on a surface at a depth of 1100 m, showing the broad lateral extent of the Loihi plume. In some cases, bottle data were interpolated to 1100-m deep surface. The contour interval is 1% in δ(^{3}He); the accuracy of the measurements is 0.25% (1σ). This figure includes data from eight different expeditions spanning the time interval from 1985 to 1994. Although these data are not synoptic, the sampling period is relatively short compared with the time scale for circulation at this depth. Helium data along WOCE lines P4 and P16 were provided by W. Jenkins (*4*, *23*).

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Lupton, 1996

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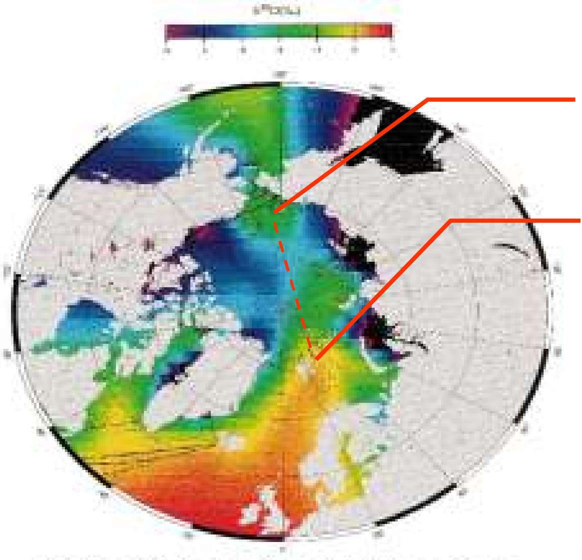
Freshwater Balance in the Arctic Ocean

Use salt, δ^{18}O, and nutrients to separate the contributions of water sources (Atlantic, Pacific, river, sea-ice melt)



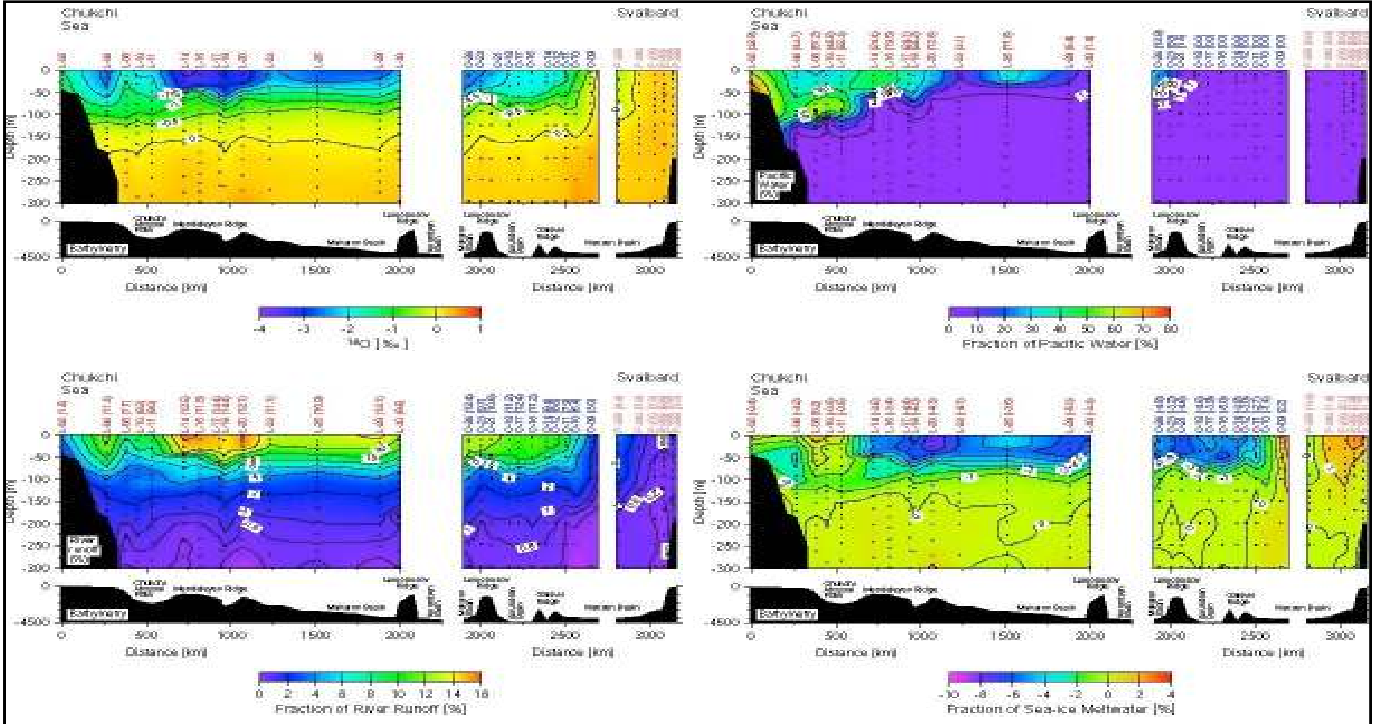
Schlosser et al., 1999

Figure 3. Mean annual discharge and δ^{18}O data available in the literature for Arctic Rivers. River discharge (km^3 yr^{-1}) is proportional to triangle size and is noted in parenthesis within or near the triangle symbol for the river [*Becker*, 1995; *Pavlov et al.*, 1996]. The negative numbers within or near the triangle symbol for each river are the δ^{18}O (‰) values [*Macdonald et al.*, 1989; *Letolle et al.*, 1993; *Ekwurzel*, 1998].

Ekwurzel et al., 2001

$$f_a + f_p + f_r + f_i = 1,$$
$$f_a S_a + f_p S_p + f_r S_r + f_i S_i = S_m,$$
$$f_a \delta^{18}\mathrm{O}_a + f_p \delta^{18}\mathrm{O}_p + f_r \delta^{18}\mathrm{O}_r + f_i \delta^{18}\mathrm{O}_i = \delta^{18}\mathrm{O}_m,$$
$$f_a \mathrm{PO_4}^*{}_a + f_p \mathrm{PO_4}^*{}_p + f_r \mathrm{PO_4}^*{}_r + f_i \mathrm{PO_4}^*{}_i = \mathrm{PO_4}^*{}_m,$$

Our mixing equations!



P. Schlosser

Examples of Stable Isotopes in Oceanography

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Oceanic $\delta^{18}O$-H_2O ($\delta^{18}O$)

- $\delta^{18}O$ follows the water molecules (not O_2!)
  - Thus, excellent stable, conservative (SC) water mass tracer
- In seawater:

$$H_2{}^{16}O / H_2{}^{18}O \approx 500/1$$

- $H_2{}^{16}O$ evaporation favored over $H_2{}^{18}O$ evaporation

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Rayleigh Distillation - Global Hydrological Cycle

- Equilibrium fractionation when water molecules evaporate from sea surface
- Equilibrium fractionation when water molecules condense from vapor to liquid (rain is heavier than vapor)
- Vapor becomes progressively lighter (i.e., δD and $\delta^{18}O$ get lower) with distance from source

- Evaporation from ocean creates depleted clouds
- Air mass transported to higher latitude (cooler)
- Water lost due to rain; raindrops enriched in ^{18}O relative to cloud
- Cloud gets lighter as it moves poleward

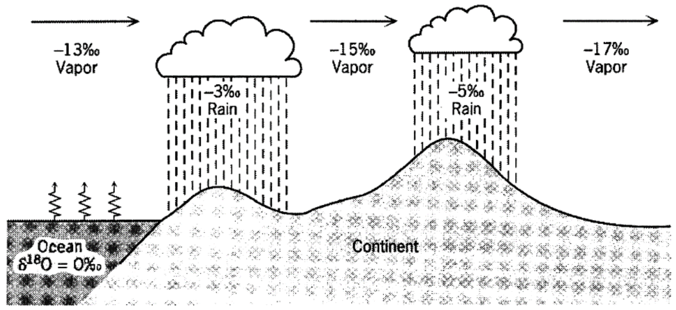
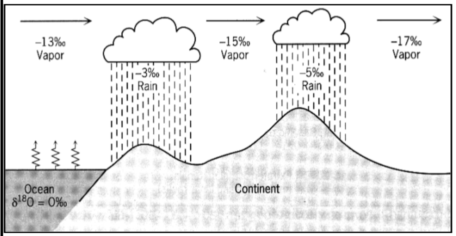
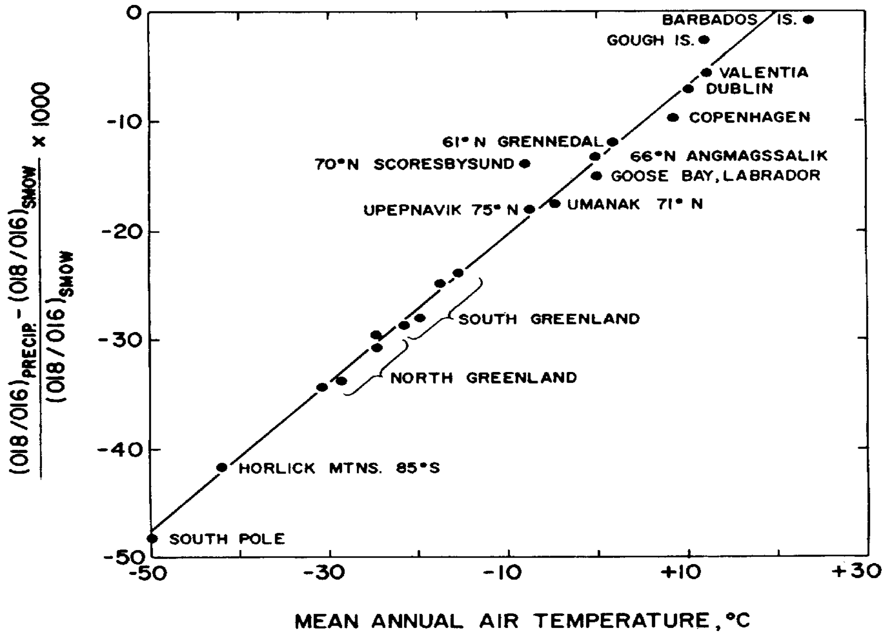


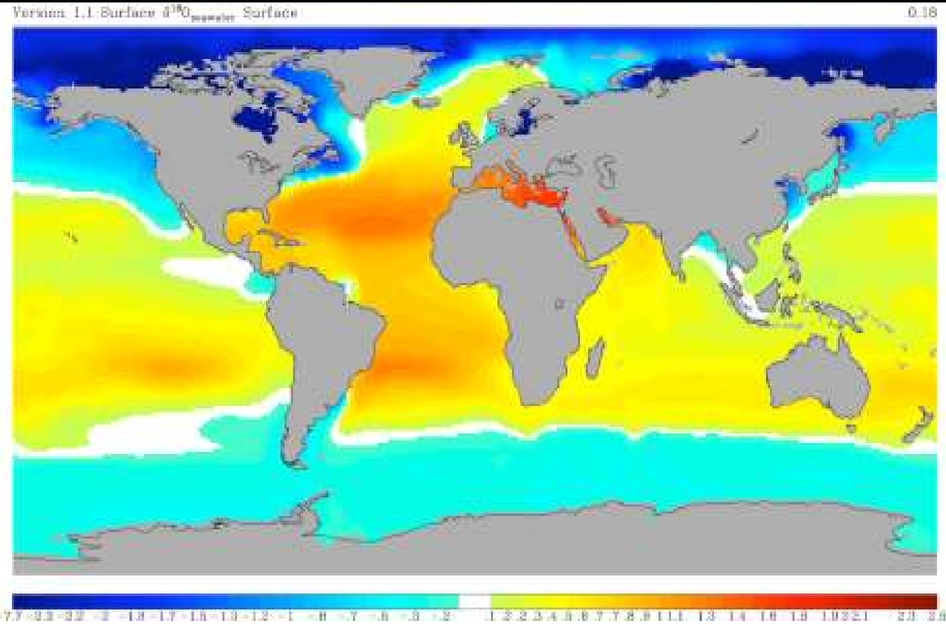
FIGURE 29.4. Schematic fractionation in the atmospheric water cycle. *Source: Lectures in Isotope Geology*, U. Siegenthaler (eds.: E. Jager and J. C. Hunziker), copyright © 1979 by Springer-Verlag, Heidelberg, Germany, p. 266.

δ^{18}O in Average Rain *vs.* Temperature, Location





Surface Seawater δ^{18}O



Higher $\delta^{18}O_{sw}$ in the net evaporation belts

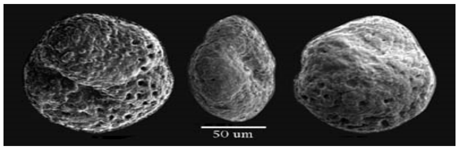
Lower $\delta^{18}O_{sw}$ at high latitudes, which are dominated by net excess precipitation

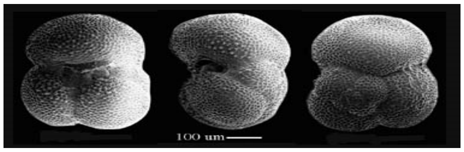
The large mass of surface seawater keeps the range from being larger

http://data.giss.nasa.gov/o18data/

Foraminiferal $\delta^{18}O$-$CaCO_3$

A Paleotemperature Recorder



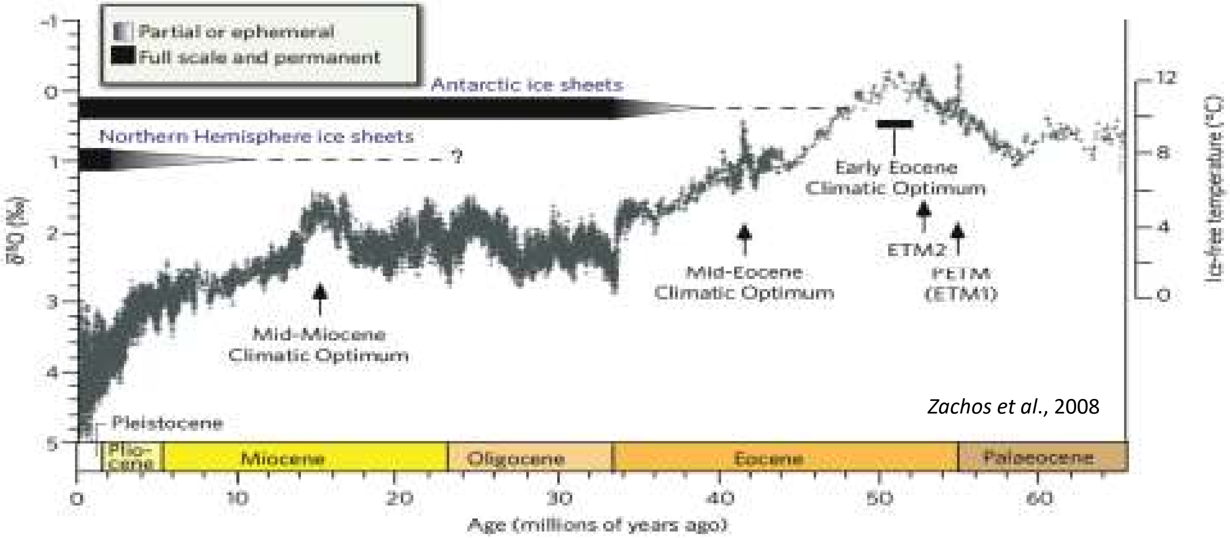


The $\delta^{18}O$ of the $CaCO_3$ is a function of:

1) Temp of seawater that forams are growing in:
   Warmer water → lighter $\delta^{18}O$-$CaCO_3$

2) $\delta^{18}O$ of seawater that forams are growing in:
   - Depends on latitude
   - Depends on glacial/interglacial state:
     - Freshwater is light compared to seawater
     - Glacial – heavier sw; Interglacial – lighter sw

$\delta^{18}O$ as Indicator of Climate for the Past 65 Ma



Zachos et al., 2008

Deep-sea benthic foraminiferal $\delta^{18}O$ curve. The $\delta^{18}O$ temperature scale was computed on the assumption of an ice-free ocean; it therefore applies only to the time preceding the onset of large-scale glaciation on Antarctica (about 35 million years ago).